Polymer pendant crown thioethers: synthesis and Hg^{II} extraction studies of a novel thiacrown polymer

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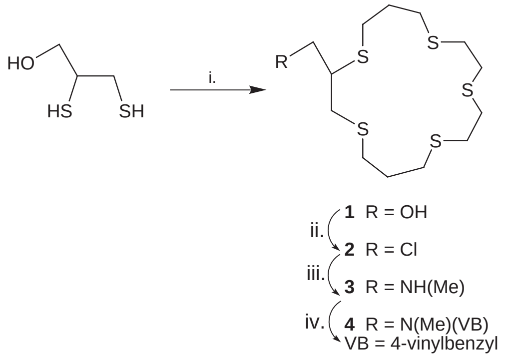
A novel C-substituted crown thioether has been synthesized and used to prepare a cross-linked polystyrene polymer containing pendant crown thioethers and that product has been shown to be effective in extracting Hg^{II} from acidic aqueous solutions.

Owing to increasing environmental concerns about waste water remediation, major efforts are under way to design new materials that can effectively remove and recover toxic metal ions from aqueous solutions. One approach to this problem has been to utilize organic ligands anchored to solid supports.[1] Specific binding properties of the ligands can be exploited to selectively remove a desired metal ion from a complex solution of cations. The utility of polymer pendant ligands for the extraction of a variety of metal ions from aqueous media has been previously demonstrated.[2]

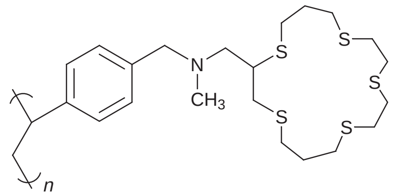
We are interested in designing polymeric materials for Hg^{II} remediation in mixed waste streams. Typically, these waste streams are not only very acidic, but also contain a wide variety of other metal ions. As a result, removal of Hg^{II} requires a robust and selective sequestering agent. To address this difficult and expensive problem, we have developed the synthesis of polymer pendant crown thioethers for the selective removal of Hg^{II} from acidic aqueous media.[3] Crown thioethers[4] are well suited for this task owing to the high affinity that sulfur crowns have for the Hg^{II} ion[5] as well as their resistance to degradation under acidic conditions.[6] As pendant ligands on solid supports, crown thioethers have been shown to remove soft metal ions, such as Ag^{I}, Hg^{II} and Pb^{II}, directly from aqueous solutions.[7] Here we present the novel synthesis of a thiacrown polymer and initial results in the extraction of the Hg^{II} ion from acidic aqueous solutions.

Preparation of thiacrown polymers first required the synthesis of a sulfur crown containing a pendant arm incorporated into the carbon framework. Functionalization of this pendant arm would allow for either the attachment of the crown to a polymer support or direct polymerization of the thiacrown monomer. While there are reported syntheses for C-substituted sulfur crowns,[7d,8] those methods were not practical for our purposes, requiring a new method for the synthesis of pendant-arm crown thioethers.

The new crown thioether, 2-hydroxymethyl-1,4,8,11,14-pentathiacycloheptadecane[9] ([17]aneS_5-OH), **1**, was synthesized in a 25% yield through reaction of 2,3-dimercaptopropan-1-ol[10] with 4,7,10-trithiatridecane-1,13-di(toluene-*p*-sulfonate) (Scheme 1), using caesium carbonate mediated cyclization.[11] Advantages of this technique are: (1) it is general for synthesizing sulfur crowns of various sizes,[12] and (2) the hydroxymethyl moiety does not need to be protected prior to the condensation reaction. [17]aneS_5-OH was then treated with thionyl chloride to form 2-chloromethyl-1,4,8,11,14-pentathiacycloheptadecane ([17]aneS_5-Cl), **2** (89%), followed by conversion to 2-(*N*-methyl)aminomethyl-1,4,8,11,14-pentathiacycloheptadecane ([17]aneS_5-NHMe), **3** (65%), through reaction with methylamine. The synthesis of the 4-vinylbenzyl-substituted thiacrown **4** (60%) was readily accomplished by treating **3** with 4-vinylbenzyl chloride. Copolymerization of the 4-vinylbenzyl-substituted thiacrown **4** with DVB (80% divinylbenzene) using AIBN as the radical initiator generated the highly cross-linked crown thioether polymer **5**.[13] Elemental analysis of the resulting polymeric material showed that each gram of the polymer contained 1.53 mmol of [17]aneS_5 crown (based on % by weight of sulfur).



Scheme 1 *Reagents and conditions*: i. $S(CH_2CH_2SCH_2CH_2CH_2OTs)_2$, Cs_2CO_3, DMF, 90 °C; ii. $SOCl_2$, CH_2Cl_2, RT; iii. $MeNH_2$, Na_2CO_3, MeCN, 0 °C; iv. 4-vinylbenzyl chloride, Na_2CO_3, MeCN, 81 °C



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Solid–liquid extraction capabilities of the polymer pendant crown thioethers were tested in aqueous solutions. Twenty milligrams of the polymer were stirred in 5 ml of a buffered solution (ammonium acetate) containing 2.0×10^{-5} g of Hg^{II} [as $Hg(NO_3)_2$] at pH 3.60. Mixing times ranged from 30 minutes to 18 hours. At the end of the mixing, the polymer powder was separated from each solution by filtering through a cotton plug. The concentration of Hg^{II} remaining in the buffer solution was quantified spectrophotometrically using a diphenylthiocarbazone extraction method adapted from the methods of Charlot.[14] Using this method, the accuracy in determining the Hg^{II} concentration was ±1 ppm. In all cases, Hg^{II} removal was determined to be 99+%, indicating the high reactivity and extraction efficiency of the thiacrown polymer. The mercury extraction performance of the polymer under different conditions (pH and Hg concentrations), in addition to metal ion competition studies, will be reported in a full paper.

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Notes and References

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9 Characterization for [17]aneS$_5$-OH (**1**)**:** mp 30–32 °C. Anal. Found (calc. for $C_{13}H_{26}OS_5$): C, 43.32 (43.57); H, 7.27 (7.32); S, 44.51 (44.65). ^{1}H NMR ($CDCl_3$) δ 1.8–2.0 (4 H, m, $CH_2C\mathit{H}_2CH_2$), 2.3 (1 H, br s, OH), 2.6–2.85 (14 H, m, $C\mathit{H}_2SC\mathit{H}_2$), 2.95 (1 H, qnt, $CH_2C\mathit{H}S$), 3.65 (1 H, dd, $HOC\mathit{H}_2CH$), 3.80 (1 H, dd, $HOC\mathit{H}_2CH$). ES-MS *m*/*z* ($C_{13}H_{26}OS_5$, 358): 357 ($M - H^+$), 417 ($M + OAc^-$) (Courtesy of Hugh Gregg, LLNL).

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12 We have also used this method to synthesize the [14]aneS$_4$-OH crown and its synthesis and characterization will be presented as part of a full paper.

13 Characterization for thiacrown polymer **5**: Anal. Found: C, 62.30; H, 7.46; N, 2.42; S, 24.51. IR (KBr, ν/cm^{-1}): 3017w, 2920s, 2848w, 1699w, 1603w, 1509w, 1437m, 1421s, 1384m, 1300m, 1259m, 1203w, 1122w, 1034m, 1018m, 922w, 825m, 799m, 711m, 567w.

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